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Thermodynamic Properties of Partially Miscible Systems: Part II—Binary Systems of Cyclohexane with Acetic Anhydride & Furfural

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The activities of components and various thermodynamic properties of mixing of binary systems of cyclohexane with acetic anhydride and furfural at 25° have been determined over the entire composition region. The data supports the earlier observations that the values of partial molar enthalpy and partial molar entropy show sharp discontinuities at compositions corresponding to maximum mutual solubilities of the components. The values of excess entropy of mixing show that the systems exhibit restriction on random mixing only where concentrations of acetic anhydride and furfural are rather high.

As an extension of our earlier[1-3] work on the thermodynamic properties of some partially miscible liquid pairs, similar results on binary systems of cyclohexane with acetic anhydride and furfural at 25° are reported in this paper. Since the components have limited mutual solubilities, the solution vapour pressures need to be determined with high accuracy. This was possible to achieve with the availability of a differential micromanometer[4-6] and a modified oil-mercury manometer[7].

Materials and Methods

Cyclohexane, acetic anhydride and furfural were purified by methods reported earlier[1]. The mutual solubilities of various liquid pairs were determined with the help of Zeiss interferometer. The solution vapour pressures were determined as reported earlier[3].

Results and Discussion

As reported earlier[3], the vapour compositions (y_1) at different values of liquid compositions (x_1) were determined by the modified incremental method[8] based on the relation

$$dy_1 = \frac{y_1(1-y_1)}{y_1-x_1} \cdot \frac{dP}{P} \qquad \ldots(1)$$

assuming the vapour phase to behave ideally. It was thus possible to evaluate the activities of the two components in each system. The values of y_1, a_1 and a_2 are given in Table 1.

Thermodynamic and excess thermodynamic properties — The values of ΔH_m at 25° were extrapolated[9] from the values[1,2] of ΔH_m at 26·9° and 48·2°. The thermodynamic properties of mixing ΔG_m and $T\Delta S_m$ were determined. For a typical case of cyclohexane (1)-furfural (2), the thermodynamic properties of mixing have been plotted in Fig. 1. The values of the various thermodynamic properties over the partially miscible region are

Table 1 — Solution Pressure, Vapour Composition and Activities of Various Systems at 25°C

x_1	P (cm)	y_1	a_1	a_2
	Cyclohexane (1)-acetic anhydride (2)			
0·0000	0·507	0·0000	0·00000	1·0000
0·0020	1·020	0·4654	0·04860	1·0755
0·0040	1·460	0·6272	0·09375	1·0735
0·0060	1·860	0·7079	0·1348	1·0716
0·0080	2·220	0·7557	0·1717	1·0698
0·0100	2·580	0·7901	0·2087	1·0680
0·0200	4·100	0·8690	0·3647	1·0595
0·0400	6·360	0·9168	0·5969	1·0442
0·0800	8·720	0·9405	0·8396	1·0234
0·1200	9·680	0·9470	0·9385	1·0113
0·1420	9·966	0·9488	0·9680	1·0068
0·9550	9·966	0·9488	0·9680	1·0068
0·9600	9·959	0·9511	0·9697	0·9599
0·9700	9·939	0·9597	0·9765	0·7902
0·9800	9·908	0·9697	0·9836	0·5929
0·9900	9·859	0·9822	0·9914	0·3456
0·9950	9·823	0·9900	0·9955	0·1945
1·0000	9·768	1·0000	1·0000	0·0000
	Cyclohexane (1)-furfural (2)			
0·0000	0·542	0·0000	0·00000	1·0000
0·0020	0·825	0·3312	0·02797	1·0181
0·0040	1·125	0·5105	0·05880	1·0159
0·0060	1·425	0·6144	0·08963	1·0139
0·0080	1·725	0·6821	0·1205	1·0118
0·0100	1·988	0·7246	0·1474	1·0099
0·0200	3·288	0·8350	0·2810	1·0006
0·0400	5·375	0·9008	0·4957	0·9839
0·0600	7·100	0·9261	0·6731	0·9685
0·0800	8·400	0·9384	0·8069	0·9555
0·1000	9·425	0·9457	0·9125	0·9441
0·1150	10·050	0·9495	0·9769	0·9362
0·9780	10·050	0·9495	0·9769	0·9362
0·9800	10·017	0·9576	0·9820	0·7840
0·9900	9·912	0·9760	0·9904	0·4396
0·9950	9·842	0·9876	0·9951	0·2257
1·0000	9·768	1·0000	1·0000	0·0000

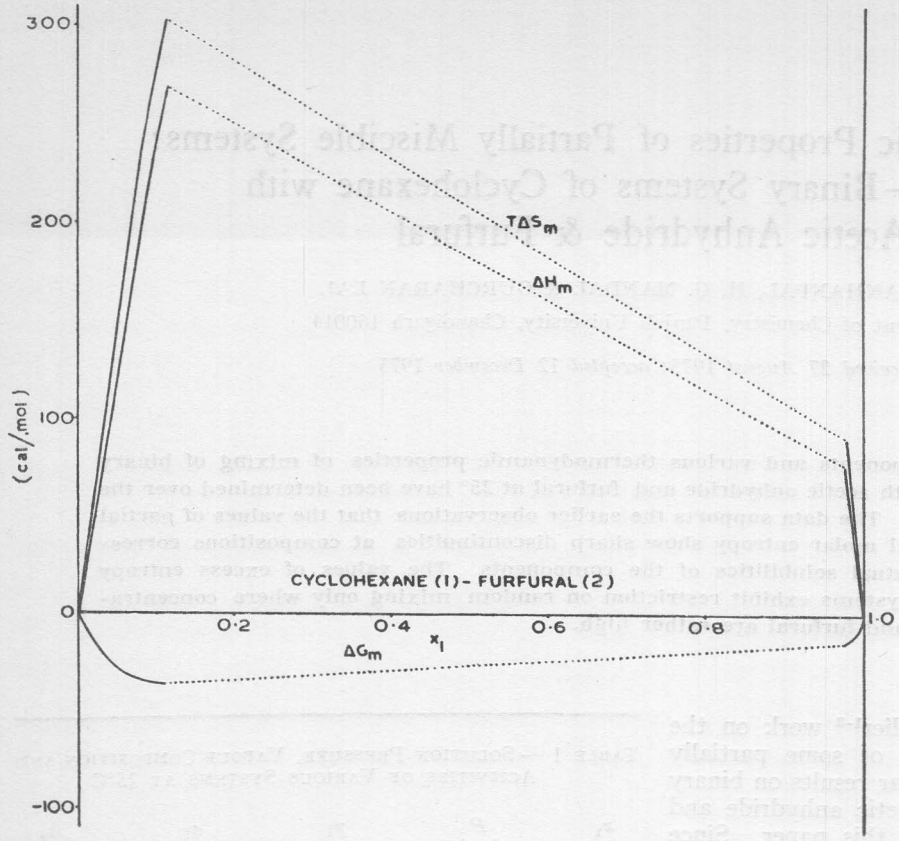

Fig. 1 — Plots of thermodynamic properties versus mole fraction of component-1 for cyclohexane (1)-furfural (2) system

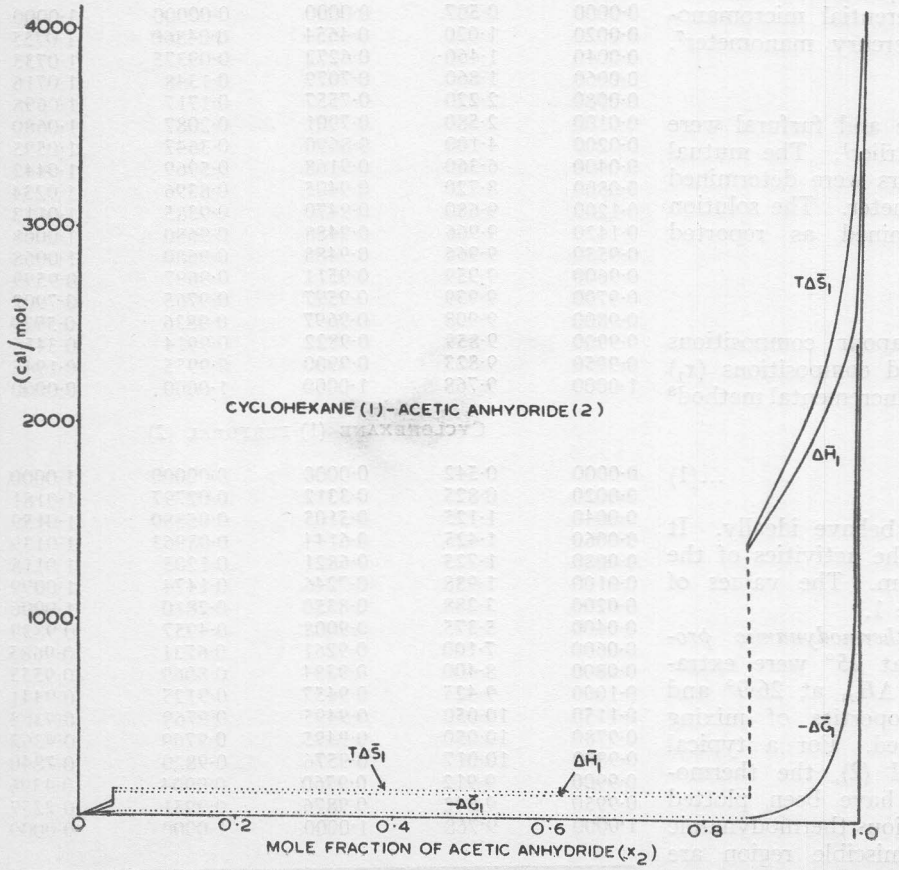

Fig. 2 — Plots of partial molar thermodynamic properties versus mole fraction of component-2 for cyclohexane (1)-acetic anhydride (2) system

TABLE 2 — VALUES OF THE DIFFERENT PARAMETERS IN EQUATION (3) FOR VARIOUS SYSTEMS AT 25°C

ΔH_m^a (cal/mole)	ΔH_m^b (cal/mole)	x_1^a	x_1^b	k	k' (cal/mole)	k^* (cal/mole)	$\Delta\bar{H}_1$ (mix) (cal/mole)	$\Delta\bar{H}_2$ (mix) (cal/mole)
CYCLOHEXANE (1)-ACETIC ANHYDRIDE (2)								
272·9	128·8	0·1420	0·9550	−1·230	144·1	−298·1	120·8	298·1
CYCLOHEXANE (1)-FURFURAL (2)								
269·7	76·04	0·1150	0·9780	−1·159	193·7	−295·6	71·1	295·6

linear functions of mole fraction, given by the relation (2)

$$\Delta X_{m\,(\text{mix})} = \frac{1}{x_1^a - x_1^b}[(\Delta X_m^a - \Delta X_m^b)x_1 + x_1^a.\Delta X_m^b - x_1^b.\Delta X_m^a] \quad \ldots(2)$$

where x_a^1 and x_1^b are the mole fractions of component-1 at saturation solubilities of component-1 in component-2 (phase a) and of component-2 in component-1 (phase b), respectively. ΔX_m^a and ΔX_m^b are the changes in the thermodynamic properties X at the compositions x_1^a and x_1^b, respectively. It may be observed that ΔH_m and $T\Delta S_m$ tend to compensate each other.

Of particular interest are the values of the excess entropy of mixing ($T\Delta S_m^E$). Unlike the partially miscible systems[3] with formic acid as one of the components, these systems show negative values of $T\Delta S_m^E$ in the phases rich in associated liquids (acetic anhydride and furfural) and positive values in the phases poorer in associated liquids. This is on account of the fact that formic acid is much more associated than acetic anhydride and furfural. It appears that acetic anhydride and furfural retain some association in solutions where their concentrations are large but readily allow random mixing of solutions where their concentrations are low.

Partial molar properties of mixing — For a typical case, cyclohexane (1)-acetic anhydride (2), the partial molar thermodynamic properties have been plotted in Fig. 2. The values of the partial molar enthalpy over the partially miscible region were calculated as reported earlier[3]. Eq. (2) for ΔH_m may be expressed as

$$\Delta H_{m\,(\text{mix})} = kk'x_1 - k'' \quad \ldots(3)$$

where

$$k = \frac{1}{x_1^a - x_1^b} \quad \ldots(4)$$

$$k' = \Delta H_m^a - \Delta H_m^b \quad \ldots(5)$$

$$k'' = (x_1^b\Delta H_m^a - x_1^a\Delta H_m^b)/(x_1^a - x_1^b) \quad \ldots(6)$$

Accordingly,

$$\Delta\bar{H}_1 = kk' - k'' \quad \ldots(7)$$

and

$$\Delta\bar{H}_2 = -k'' \quad \ldots(8)$$

The values of the various parameters k, k', k'', ΔH_m^a and ΔH_m^b are reported in Table 2 for both the systems. The results illustrated in Fig. 2 support the earlier conclusions that (i) partial molar properties remain constant over the partially miscible region of composition, (ii) except for the partial molar free energy, the partial molar enthalpy and partial molar entropy show sharp discontinuities at compositions x_1^a and x_1^b, and (iii) the values of both the partial molar enthalpy and partial molar entropy of mixing over the partially miscible range of composition lie between their values at compositions x_1^a and x_1^b corresponding to their maximum mutual solubilities.

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